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(54) Title: CHIRAL COMPOUNDS II

(57) Abstract: The invention relates to chiral compounds of formula (I)  $R^1-X^1-(A^1-Z^1)_m-G-(Z^2-A^2)_n-X^2-R^2$ , wherein  $R^1$ ,  $R^2$ ,  $X^1$ ,  $X^2$ ,  $A^1$ ,  $A^2$ ,  $Z^1$ ,  $Z^2$ ,  $G$ ,  $m$  and  $n$  have the meaning given in claim 1, to liquid crystalline mixtures comprising at least one chiral compound of formula (I), to chiral linear or crosslinked liquid crystalline polymers obtainable by polymerizing a polymerizable mixture comprising at least one chiral compound of formula (I), to the use of chiral compounds of formula (I) and mixtures and polymers obtained thereof in liquid crystal displays, active and passive optical elements, adhesives, synthetic resins with anisotropic mechanical properties, cosmetic and pharmaceutical compositions, diagnostics, liquid crystal pigments, for decorative and security applications, nonlinear optics, optical information storage or as chiral dopants, and to a liquid crystal display comprising a mixture comprising at least one chiral compound of formula (I).

## Chiral Compounds II

5 The invention relates to chiral compounds, to liquid crystalline mixtures containing the chiral compounds, to polymers obtained from the chiral compounds and liquid crystalline mixtures, and to the use of the chiral compounds, liquid crystalline mixtures and polymers obtained thereof in liquid crystal displays, active and passive optical elements like polarizers, compensators, alignment layers, colour filters or holographic elements, in adhesives, synthetic resins with anisotropic mechanical properties, cosmetic and pharmaceutical compositions, diagnostics, liquid crystal pigments, for decorative and security applications, in nonlinear optics, optical information storage or as chiral dopants.

15 Chiral compounds can be used as dopants to induce or enhance a helical twist in a liquid crystalline mixture that is used for example in liquid crystal displays. The pitch  $p$  of the molecular helix in the first approximation, which is sufficient for most practical applications, is inversely proportional to the concentration  $c$  of the chiral dopant in the liquid crystal host mixture according to equation (1) :

$$p = \frac{1}{\text{HTP}} \cdot \frac{1}{c} \quad (1)$$

25 The proportionality factor is the helical twisting power (HTP) of the chiral dopant.

For many applications it is desirable to have LC mixtures with a twisted phase. Among these are e.g. phase-change displays, guest-host displays, passive and active matrix TN and STN displays like AMD-TN, ferroelectric displays and cholesteric displays like SSCT (surface stabilized cholesteric texture) or PSCT (polymer stabilized cholesteric texture) displays, including displays with temperature compensated characteristics, e.g. by appropriate selection of the cholesteric compounds according to the invention either alone or in combination with further chiral dopants. For these applications it is

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advantageous to have available a chiral dopant with a high HTP in order to reduce the amount of dopant needed to induce the desired pitch.

5 For some applications it is desired to have LC mixtures that exhibit a strong helical twist and thereby a short pitch length. For example in liquid crystalline mixtures that are used in selectively reflecting cholesteric displays like SSCT or PSCT, the pitch has to be selected such that the maximum of the wavelength reflected by the cholesteric helix is in the  
10 range of visible light. Another possible application are polymer films with a chiral liquid crystalline phase for optical elements, such as cholesteric broadband polarizers or chiral liquid crystalline retardation films.

15 As can be seen from equation (1), a short pitch can be achieved by using high amounts of dopant or by using a dopant with a high HTP.

Chiral compounds are disclosed for example in WO 95/16007, WO 98/00428 and GB 2 328 207 A.

20 However, the chiral dopants of prior art often exhibit low values of the HTP, so that high amounts of dopant are needed. This is a disadvantage because chiral dopants can be used only as pure enantiomers and are therefore expensive and difficult to synthesize.

25 Furthermore, when using chiral dopants of prior art in high amounts, they often negatively affect the properties of the liquid crystalline host mixture, such as e.g. the clearing point, the dielectric anisotropy  $\Delta\epsilon$ , the viscosity, the driving voltage or the switching times.

30 Another disadvantage of prior art chiral compounds is that they often show low solubility in the liquid crystal host mixture, which leads to undesired crystallization at low temperatures. To overcome this disadvantage, typically two or more different chiral dopants have to be added to the host mixture. This implies higher costs and also  
35 requires additional effort for temperature compensation of the

mixture, as the different dopants have to be selected such that their temperature coefficients of the twist compensate each other.

Consequently, there is a considerable demand for chiral compounds with a high HTP which are easy to synthesize, can be used in low amounts, show improved temperature stability of the cholesteric pitch e.g. for utilizing a constant reflection wavelength, do not affect the properties of the liquid crystalline host mixture and show good solubility in the host mixture.

The invention has the aim of providing chiral compounds having these properties, but which do not have the disadvantages of the chiral dopants of the state of the art as discussed above.

Another aim of the invention is to extend the pool of chiral compounds that can be used as dopants available to the expert.

It has been found that these aims can be achieved by providing chiral compounds of formula I.

$$R^1-X^1-(A^1-Z^1)_m-G-(Z^2-A^2)_n-X^2-R^2 \quad I$$

wherein

$R^1$  and  $R^2$  are independently of each other F, Cl, Br, CN, SCN,  $SF_5$ , or a chiral or achiral alkyl group with up to 30 C atoms which may be unsubstituted, mono- or polysubstituted by F, Cl, Br or CN, it being also possible for one or more non-adjacent  $CH_2$  groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH<sub>3</sub>)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or a polymerizable group,

$X^1$ ,  $X^2$ ,  $Z^1$  and  $Z^2$  are independently of each other -O-, -S-, -CO-,

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5                   -COO-, -OCO-, -O-COO-, -CO-N(R<sup>3</sup>)-, -N(R<sup>3</sup>)-CO-,  
                   -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -SCH<sub>2</sub>-, -CH<sub>2</sub>S-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-,  
                   -CF<sub>2</sub>S-, -SCF<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-,  
                   -CF<sub>2</sub>CF<sub>2</sub>-, -CH=CH-, -CF=CH-, -CH=CF-, -CF=CF-,  
                   -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

R<sup>3</sup>               is H or alkyl with 1 to 4 C atoms,

10           A<sup>1</sup> and A<sup>2</sup>   are independently from one another 1,4-phenylene in  
                   which, in addition, one or more CH groups may be  
                   replaced by N, 1,4-cyclohexylene in which, in addition,  
                   one or two non-adjacent CH<sub>2</sub> groups may be replaced by  
                   O and/or S, 1,3-dioxolane-4,5-diyl, 1,4-cyclohexenylene,  
 15           1,4-bicyclo-(2,2,2)-octylene, piperidine-1,4-diyl,  
                   naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl,  
                   1,2,3,4-tetrahydronaphthalene-2,6-diyl or indane-2,5-  
                   diyl, it being possible for all these groups to be  
                   unsubstituted, mono- or polysubstituted with halogen,  
                   cyano or nitro groups or alkyl, alkoxy, alkylcarbonyl or  
 20           alkoxycarbonyl groups with 1 to 7 C atoms, wherein one  
                   or more H atoms may be substituted by F or Cl,

m and n       are independently of each other 0, 1, 2, 3 or 4, and

25           G           is a chiral group,

                  wherein at least one of X<sup>1</sup>, X<sup>2</sup>, Z<sup>1</sup> and Z<sup>2</sup> is -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CF<sub>2</sub>S-,  
                   -SCF<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CH=CF-, -CF=CH- or -CF=CF-.

30           Another object of the invention is a liquid crystalline mixture  
                   containing at least one compound of formula I.

                  Another object of the present invention is a polymerizable liquid  
                   crystalline mixture comprising at least one compound of formula I  
 35           and at least one polymerizable mesogenic compound having at least  
                   one polymerizable functional group.

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Another object of the invention is a chiral linear or crosslinked liquid crystalline polymer obtainable by polymerizing a polymerizable liquid crystalline mixture comprising one or more compounds of formula I.

5

A further object of the invention is the use of a chiral compound, mixture or polymer as described above in liquid crystal displays, such as STN, TN, AMD-TN, temperature compensation, ferroelectric, guest-host, phase change or surface stabilized or polymer stabilized cholesteric texture (SSCT, PSCT) displays, in active and passive optical elements like polarizers, compensators, alignment layers, colour filters or holographic elements, in adhesives, synthetic resins with anisotropic mechanical properties, cosmetic and pharmaceutical compositions for example as UV filters, diagnostics, liquid crystal pigments, for decorative and security applications, in nonlinear optics, optical information storage or as chiral dopants.

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Yet another object of the invention is a liquid crystal display comprising a liquid crystalline mixture or a polymerizable liquid crystalline mixture comprising at least one chiral compound of formula I.

20

The inventive chiral compounds bear several advantages

- they exhibit a good solubility in liquid crystalline mixtures,
- they exhibit broad liquid crystalline phases,
- by varying the chiral group  $R^1$  and/or  $R^2$  compounds with a high twisting power  $HTP$  can be obtained,
- when inventive compounds are used as chiral dopant in a liquid crystalline mixture, due to their high solubility higher amounts of dopant can be used to produce a high twist (= a low pitch),
- in case high amounts of dopants are needed, due to the broad liquid crystalline phases of the inventive dopants the liquid crystal phase of the host mixture is less negatively influenced,

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30

35

- in case of inventive compounds with high HTP, lower amounts are needed to achieve a high pitch, and thereby the liquid crystalline properties of the mixture are less negatively affected,
- 5 • enantiomerically pure chiral compounds are easy to prepare from cheap, readily available starting materials,
- both the R and S enantiomers can be prepared, which allows the formation of a cholesteric phase with either a right or left handed cholesteric helix,
- 10 • the availability of both helices is a considerable advantage, e.g. for the use in security applications, as it enables the production of chiral films or coatings reflecting circularly polarized light of a single handedness.

15 The inventive chiral compounds are mesogenic or even liquid crystalline, i.e. they can induce or enhance mesophase behaviour for example in admixture with other compounds, or even exhibit one or more mesophases themselves. It is also possible that the inventive compounds show mesophase behaviour only in mixtures with other  
20 compounds, or, in case of polymerizable compounds, when being (co)polymerized. Mesogenic inventive chiral compounds are especially preferred.

25 The groups  $R^1$ ,  $R^2$ ,  $X^1$ ,  $X^2$  and the mesogenic groups  $(A^1-Z^1)_m$  and  $(A^2-Z^2)_n$  on both sides of G can be identical or different. A preferred embodiment of the invention is directed to compounds wherein the mesogenic groups on both sides of G are different.

30 Very preferred are compounds wherein at least one of  $Z^1$  and  $Z^2$  is - $CF_2O$ -, - $OCF_2$ -, - $CF_2S$ -, - $SCF_2$ - or - $CF_2CF_2$ -. Further preferred are compounds wherein at least one of  $X^1$  and  $X^2$  is - $CF_2O$ - or - $OCF_2$ -. Further preferred are compounds wherein at least one of  $X^1$ ,  $X^2$ ,  $Z^1$  and  $Z^2$  is - $CF_2O$ -, - $OCF_2$ -, - $CF_2S$ -, - $SCF_2$ -, - $CF_2CF_2$ - or - $CF=CF$ - and the other are - $COO$ -, - $OCO$ -, - $CH_2-CH_2$ - or a single bond.

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Another preferred embodiment relates to compounds wherein at least one of  $Z^1$  and  $Z^2$  denotes  $-C\equiv C-$ . These compounds are especially suitable for uses where highly birefringent materials are needed.

5

Further preferred are compounds of formula I wherein the mesogenic groups  $(A^1-Z^2)_m$  and  $(A^2-Z^2)_n$  incorporate one, two or three, especially two five- or six-membered rings.

10

Particularly preferred compounds are those wherein  $m$  and  $n$  are 1 or 2 and  $A^1$  and  $A^2$  are selected of 1,4-phenylene and trans-1,4-cyclohexylene, these rings being unsubstituted or substituted in 1 to 4 positions with F, Cl, CN or alkyl, alkoxy, alkylcarbonyl or

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alkoxycarbonyl with 1 to 4 C-atoms. From these preferred compounds, especially preferred are those comprising a bicyclohexyl or cyclohexylphenyl group.

20

A smaller group of preferred mesogenic groups  $(A^1-Z^1)_m$  and  $(A^2-Z^2)_n$  is listed below. For reasons of simplicity, Phe in these groups is 1,4-phenylene which may also substituted by at least one group L, with L being F, Cl, CN or an optionally fluorinated alkyl, alkoxy, alkylcarbonyl or alkoxycarbonyl group with 1 to 4 C atoms, Cyc is 1,4-cyclohexylene and Z has in each case independently one of the meanings of  $Z^1$  in formula I. The list of preferred mesogenic groups is

25

	-Phe-	II-1
	-Cyc-	II-2
	-Phe-Z-Phe-	II-3
30	-Phe-Z-Cyc-	II-4
	-Cyc-Z-Cyc-	II-5
	-Phe-Z-Phe-Z-Phe-	II-6
	-Phe-Z-Phe-Z-Cyc-	II-7
	-Phe-Z-Cyc-Z-Phe-	II-8
35	-Cyc-Z-Phe-Z-Cyc-	II-9
	-Cyc-Z-Cyc-Z-Phe-	II-10



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-Cyc-Z-Cyc-Z-Cyc-

II-11

Particularly preferred are the subformulae II-3, II-4, II-5, II-6, II-7 and II-10, in particular II-4 and II-5.

5

Further preferred are subformula II-5, wherein Z is  $-\text{CF}_2\text{CF}_2-$  and subformula II-3 and II-4, wherein Z is  $-\text{OCF}_2-$ .

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Further preferred are subformulae II-10 and II-11, wherein one or both of Z between two cyclohexylene rings are  $-\text{CF}_2\text{CF}_2-$ , and subformulae II-6, II-7, II-8, II-9, and II-10, wherein one or both of Z between two phenylene rings or between a phenylene and a cyclohexylene ring are  $-\text{OCF}_2-$  or  $-\text{CF}_2\text{O}-$ , with the O atom being adjacent to the phenylene ring.

15

The other groups Z are preferably  $-\text{COO}-$ ,  $-\text{OCO}-$ ,  $-\text{CH}_2\text{CH}_2-$  or a single bond.

20

Bi- and tricyclic mesogenic groups are preferred. Further preferred are compounds wherein the mesogenic group comprises at least one group Phe that is substituted with one or two groups L, preferably in 3- and/or 5-position, and L is F, Cl,  $\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{CF}_3$ ,  $\text{CHF}_2$ ,  $\text{CH}_2\text{F}$ ,  $\text{OCF}_3$ ,  $\text{OCHF}_2$ ,  $\text{OCH}_2\text{F}$  or CN.

25

L is preferably F, Cl, CN,  $\text{NO}_2$ ,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$ ,  $\text{COCH}_3$ ,  $\text{COC}_2\text{H}_5$ ,  $\text{CF}_3$ ,  $\text{CHF}_2$ ,  $\text{CH}_2\text{F}$ ,  $\text{OCF}_3$ ,  $\text{OCHF}_2$ ,  $\text{OCH}_2\text{F}$ ,  $\text{OC}_2\text{F}_5$ , in particular F, Cl, CN,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{OCH}_3$ ,  $\text{CF}_3$  and  $\text{OCF}_3$ , most preferably F,  $\text{CH}_3$ ,  $\text{CF}_3$ ,  $\text{OCH}_3$  and  $\text{OCF}_3$ .

30

If  $\text{R}^1$  or  $\text{R}^2$  in formula I is an alkyl or alkoxy radical, i.e. where the terminal  $\text{CH}_2$  group is replaced by  $-\text{O}-$ , this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

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